

## A Chemical Modification of a $\text{Mn}_{12}$ Single-Molecule Magnet by Replacing Carboxylate Anions with Diphenylphosphate Anions

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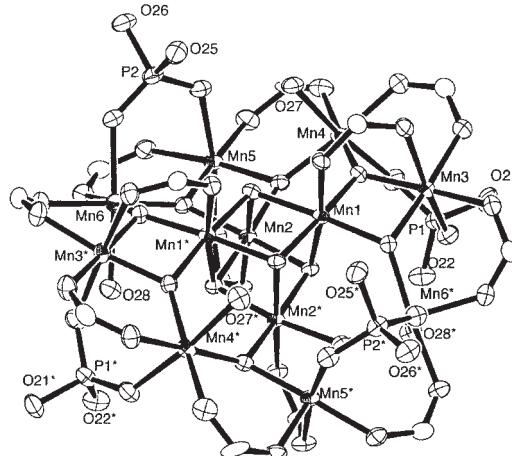
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Diphenylphosphate anions can replace with benzoate anions of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$  to afford a novel  $\text{Mn}_{12}$  single-molecule magnet (SMM) with mixed bridging ligands.

A large spin ground state ( $S$ ) together with a negative magnetic anisotropy ( $D$ ) are the essential features for a molecule to function as a single-molecule magnet (SMM).<sup>1</sup> A twelve-nuclei manganese complex  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CMe})_{16}(\text{H}_2\text{O})_4]$  (**1**) is one of the most extensively-studied SMM with  $S = 10$  and  $D = -0.5$  K.<sup>1</sup> Chemical modifications so far done for this complex include substitutions of bridging acetates to other carboxylates<sup>1,2</sup> and partial substitutions of a peripheral Mn(III) ion to a Fe(III)<sup>3</sup> or a Cr(III)<sup>4</sup> ion. The characterization of their structures together with their magnetic properties enabled the investigation about the origin of the appearance of two responses in ac magnetic susceptibility.<sup>2a,2b</sup> A substitution of carboxylate anions to non-carboxylate oxo anions would expand the possibility of chemical modification in  $\text{Mn}_{12}$  complexes. Here we report a partial substitution of benzoate anions in  $\text{Mn}_{12}$ -benzoate to phosphate anions to afford a novel  $\text{Mn}_{12}$  complex with mixed bridging anions. Partial substitutions of carboxylate anions to non-carboxylate anions such as nitrates<sup>5</sup> or phosphinate<sup>6</sup> have been reported recently by Christou et al., which revealed these substitutions affect a little on the magnetic properties.

Reaction of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4]$  with 4 equiv of  $(\text{PhO})_2\text{PO}_2\text{H}$  in  $\text{CH}_2\text{Cl}_2$  followed by addition of hexane leads to black crystals of  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{12}(\text{O}_2\text{P}(\text{OPh})_2)_4(\text{H}_2\text{O})_4]$  (**2**) after a week. Single crystal X-ray structure analysis<sup>7</sup> revealed that **2** crystallizes in the monoclinic space group  $P2/n$  with four solvent molecules giving the formula of **2**·4 $\text{CH}_2\text{Cl}_2$ . Figure 1 shows the molecular structure of **2** together with the atom numbering scheme for selected atoms. The  $\text{Mn}_{12}\text{O}_{12}$  core structure is almost the same as that of **1**: the central  $[\text{Mn}_4^{\text{IV}}\text{O}_4]^{8-}$  cubane and the outer ring of eight  $\text{Mn}^{\text{III}}$  ions connected by eight  $\mu^3\text{-O}^{2-}$  bridges. The peripheral bridging ligands are categorized in three groups. They are eight equatorial benzoate, four axial benzoate, and four axial phosphates. The axial benzoate groups are bridging  $\text{Mn}^{\text{IV}}$  and  $\text{Mn}^{\text{III}}$  ions whereas the phosphates are bridging two  $\text{Mn}^{\text{III}}$  ions. The arrangement of four coordinated water molecules is the 1 : 1 : 1 : 1 fashion with alternating up and down positions. Four water oxygen atoms are involved in the elongated Mn-O bonds. The eight Jahn-Teller axes of Mn(III) ions are roughly parallel to the crystallographic *b*-axis with angles of 15–38°. This is consistent with the observation of only a high-temperature (HT) phase in the ac magnetization measurement (vide infra). The yield of **2** in crystalline form was ca. 30%. The same procedure with 8 equiv of  $(\text{PhO})_2\text{PO}_2\text{H}$  leads to no crystals

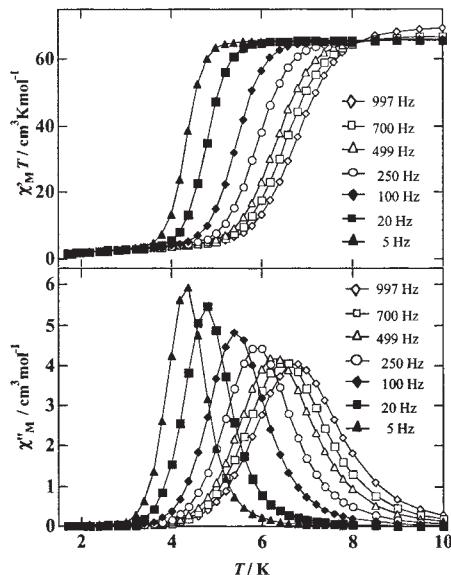
nor precipitates.



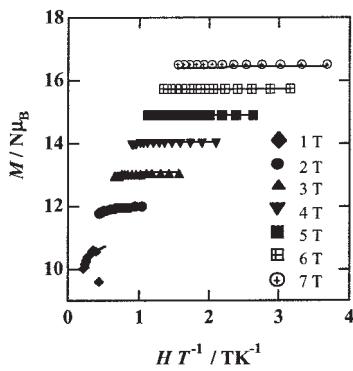
**Figure 1.** An ORTEP view of **2** with atom numbering scheme for selected atoms. Phenyl groups and hydrogen atoms of water molecules are omitted for clarity.

The ac magnetic susceptibility of polycrystalline sample of **2** was measured at seven frequencies (5–997 Hz) for the temperature range of 1.7–10.0 K. As expected for SMM,<sup>1</sup> **2** shows frequency-dependent ac out-of-phase signals as shown in Figure 2. The frequency dependence of the  $\chi''_M$  peak temperature can be analyzed by the Arrhenius law.<sup>1</sup> On the basis of the plots of the natural logarithm of the relaxation time  $\tau$  evaluated by  $1/(2\pi\nu)$ , where  $\nu$  is the ac frequency, vs the inverse of the  $\chi''_M$  peak temperature  $T$ , the effective energy barrier ( $U_{\text{eff}}$ ) for magnetization relaxation and pre-exponential factor  $\tau_0$  were estimated to be 64.2 K and  $1.21 \times 10^{-8}$  s, respectively. The former value is comparable to those of the HT phases of the other  $\text{Mn}_{12}$  complexes.<sup>1,2</sup>

In order to estimate the ground spin state ( $S$ ) and the magnitude of the zero-field splitting ( $D$ ), dc magnetization data were collected in the temperature range of 1.9–4.5 K and at external fields of 1.0–7.0 T for polycrystalline sample of complex **2**. The sample was restrained in eicosane matrix to prevent torquing at high fields. The observed magnetization data  $M/(N\mu_B)$  were plotted vs  $H/T$  in Figure 3, which were fitted with a magnetization fitting program “*axfit*”<sup>8</sup> assuming an  $S = 10$  ground state. The lines in Figure 3 show the fitting with the parameters of  $g = 1.92$  and  $D = -0.63$  K. The deviation of experimental data from the line at low temperatures with 1 T external field is probably due to the blocking of the magnetization. By using  $D = -0.63$  K and  $S = 10$ , we can estimate the energy barrier for magnetization relaxation  $U = |D|S_z^2$  as 63 K, which is



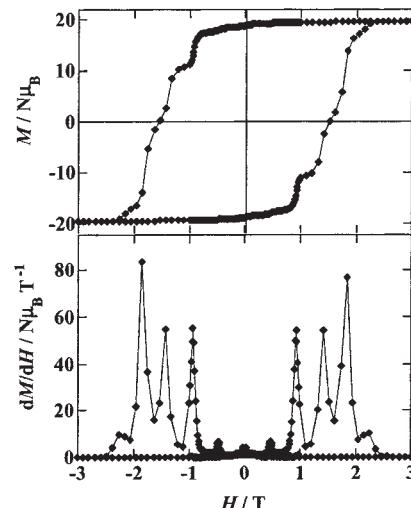
**Figure 2.** Ac magnetic susceptibility data for **2** in the form of  $\chi'_M T$ - $T$  (top) and  $\chi''_M$ - $T$  (bottom) plots.



**Figure 3.** Reduced magnetization data for **2** at different external fields. Lines show the best-fit assuming  $S = 10$ .

comparable to the effective energy barrier  $U_{\text{eff}}$  of 64.2 K obtained by ac susceptibility measurements.

The magnetization hysteresis loop measured for the oriented single crystals of **2** at 1.9 K is shown in Figure 4. Crystals in eicosane matrix were aligned by a 7.0 T field at 325 K for 5 min, then the temperature was gradually decreased to solidify the eicosane. In this way we could measure hysteresis loops with the external magnetic field applied parallel to the easy axis of magnetization. The magnetization saturates completely at fields above 2.3 T to ca.  $20 N\mu_B$ . Hysteresis is seen with a coercive field of 1.5 T. In the lower part of Figure 4 is shown the first derivative of the hysteresis plot. As the field is decreased from +3 T, the first step can be seen at zero field, followed by steps at  $-0.47$ ,  $-0.93$ ,  $-1.42$ ,  $-1.84$ , and  $-2.26$  T. The steps correspond to increases in the rate of change of the magnetization, and are attributable to resonant tunneling between quantum spin states.<sup>9</sup> The step interval  $\Delta H$  in a hysteresis loop is given as  $\Delta H = -nD/(g\mu_B)$ , where  $n = 0, 1, 2, \dots$  Using the observed  $\Delta H$  of 0.46 T for **2**, we can estimate the value  $|D|/g$  to be 0.31 K, which is fairly comparable to 0.33 K calculated by using the  $g$  and  $D$  values obtained from the reduced magnetization experiment.



**Figure 4.** A magnetization hysteresis loop for oriented crystals of **2** measured in an eicosane matrix at 1.9 K (top) and the corresponding first derivatives  $dM/dH$  (bottom).

The obtained parameters,  $S$ ,  $D$ ,  $g$ , and  $U_{\text{eff}}$ , are within the range of those for  $\text{Mn}_{12}$  derivatives reported so far, indicating the partial substitution of carboxylate anions to phosphate anions does not cause a serious effects on the structure and on the magnetic property.

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#### References and Notes

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